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Organic, elemental and inorganic carbon in particulate matter of six urban environments in Europe

M. Sillanpää¹, A. Frey¹, R. Hillamo¹, A. S. Pennanen², and R. O. Salonen²

¹Finnish Meteorological Institute, Air Quality Research, Erik Palménin aukio 1, FIN-00560 Helsinki, Finland

²National Public Health Institute, Department of Environmental Health, Neulaniementie 4, FIN-70210 Kuopio, Finland

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Abstract. A series of 7-week sampling campaigns were conducted in urban background sites of six European cities as follows: Duisburg (autumn), Prague (winter), Amsterdam (winter), Helsinki (spring), Barcelona (spring) and Athens (summer). The campaigns were scheduled to include seasons of local public health concern due to high particulate concentrations or findings in previously conducted epidemiological studies. Aerosol samples were collected in parallel with two identical virtual impactors that divide air particles into fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) size ranges. From the collected filter samples, elemental (EC) and organic (OC) carbon contents were analysed with a thermal-optical carbon analyser (TOA); total Ca, Ti, Fe, Si, Al and K by energy dispersive X-ray fluorescence (ED-XRF); As, Cu, Ni, V, and Zn by inductively coupled plasma mass spectrometry (ICP/MS); Ca^{2+} , succinate, malonate and oxalate by ion chromatography (IC); and the sum of levoglucosan+galactosan+mannosan (ΣMA) by liquid chromatography mass spectrometry (LC/MS). The campaign means of $PM_{2.5}$ and $PM_{2.5-10}$ were $8.3\text{--}29.6\ \mu\text{g m}^{-3}$ and $5.4\text{--}28.7\ \mu\text{g m}^{-3}$, respectively. The contribution of particulate organic matter (POM) to $PM_{2.5}$ ranged from 21% in Barcelona to 54% in Prague, while that to $PM_{2.5-10}$ ranged from 10% in Barcelona to 27% in Prague. The contribution of EC was higher to $PM_{2.5}$ (5–9%) than to $PM_{2.5-10}$ (1–6%) in all the six campaigns. Carbonate ($C(CO_3)$), that interferes with the TOA analysis, was detected in $PM_{2.5-10}$ of Athens and Barcelona but not elsewhere. It was subtracted from the OC by a simple integration method that was validated. The $CaCO_3$ accounted for 55% and 11% of $PM_{2.5-10}$ in Athens and Barcelona, respectively. It was anticipated that combustion emissions from vehicle engines affected the POM con-

tent in $PM_{2.5}$ of all the six sampling campaigns, but a comparison of mass concentration ratios of the selected inorganic and organic tracers of common sources of organic material to POM suggested also interesting differences in source dominance during the campaign periods: Prague (biomass and coal combustion), Barcelona (fuel oil combustion, secondary photochemical organics) and Athens (secondary photochemical organics). The on-going toxicological studies will clarify the health significance of these findings.

1 Introduction

Urban aerosol is a complex mixture of primary particulate emissions (from industry, transportation, power generation and natural sources) and secondary material formed by gas-to-particle conversion mechanisms. Urban aerosol contains a substantial amount of carbonaceous material (20–80%; Rogge et al., 1993 and Nunes and Pio, 1993) that is composed of two main fractions: 1) elemental carbon (EC; sometimes referred to as black carbon or graphitic carbon) is a primary pollutant formed in combustion processes, and 2) particulate organic matter (POM) is a complex mixture of different groups of compounds originating from a large variety of processes (Seinfeld and Pandis, 1998).

Recent epidemiological studies have shown consistent associations of mass concentration of urban air thoracic particles (PM_{10} – 50% cutoff point at $10\ \mu\text{m}$), and its subfraction fine particles ($PM_{2.5}$ – 50% cutoff point at $2.5\ \mu\text{m}$), with mortality and morbidity among cardiorespiratory patients (WHO, 2003). There are still relatively few epidemiological studies with detailed chemical speciation of the collected particulate samples, but one recent US time-series study (Metzger et al., 2004) has reported that the EC and

Correspondence to: M. Sillanpää
(markus.sillanpaa@fini.fi)

POM concentrations in PM_{2.5} were significantly associated with emergency department visits in hospitals due to cardiovascular diseases. It is known on the basis of experimental studies that the EC causes tissue irritation and a release of toxic chemical intermediates from scavenger cells in laboratory studies as well as acts as a carrier of various organic compounds. Moreover, volatile and semi-volatile organic, particulate-bound compounds can act as irritants and allergens. Many aromatic compounds are suspected mutagens and carcinogens and some of them may also cause acute health effects (Lighty et al., 2000).

In this study, we report the mass concentrations of fine (PM_{2.5}) and coarse (PM_{2.5–10}) particles as well as their EC and POM contents from six geographically and seasonally contrasting particulate sampling campaigns in Europe. The campaigns were scheduled to include seasons of local public health concern due to high particulate concentrations or findings in previously conducted epidemiological studies. A specific objective of our work was to characterise the differences in concentration patterns as well as sources of the EC and POM between the sampling campaigns. Moreover, a new integration method was validated for subtraction of carbonate (C(CO₃)) from the thermograms of the thermal-optical carbon analysis.

2 Experimental methods

2.1 Sampling sites

A series of 7-week sampling campaigns were conducted in six European cities. The sampling sites were located in urban background areas and were influenced by a variable contribution of traffic depending on the density of short-haul motor vehicles and the site topography. The sites are described in detail including the additional local emission sources of particles:

Duisburg (51°26' N, 6°45' E). The sampling site was located near the city centre at a distance of 280 m from the nearest major street. The site was surrounded by three to five-storey buildings. The major local emission sources were road traffic (e.g. diesel trucks) and metal industry. The sampling campaign was conducted between 4 October and 21 November 2002 (autumn) when the mean±SD ambient temperature and total precipitation were 9±3°C and 90 mm.

Prague (50°5' N, 14°26' E). The sampling site was located in an open field of the Czech Hydrometeorological Institute in an uptown residential area. The nearest road at a distance of 150 m had a relatively low average traffic density of 5000 vehicles/day, while the nearest major road was at a distance of 1 km. Road traffic, domestic heating with solid fuels and energy production were considered as the main local emission sources. The particulate samplings were carried out between 29 November 2002 and 16 January 2003 (winter) with

prevailing ambient temperature of −2±5°C and total precipitation of 50 mm.

Amsterdam (52°21' N, 4°54' E). The site was located near the city centre at a distance of 50 m from the nearest major street with an average traffic volume of 10 000 vehicles/day. The site was surrounded by multi-storey buildings. Road and ship traffic were considered as the main local emission sources. The sampling campaign was conducted between 24 January and 13 March 2003 (winter) when the ambient temperature and total precipitation were 4±4°C and 60 mm.

Helsinki (60°10' N, 24°58' E). The site was located near the city centre at a distance of 300 m from the nearest major street with an average traffic volume of 30 700 vehicles/day. The site had multi-storey buildings on one side but faced an open sports field on the other side. Road traffic and ships in the city harbour were considered as the main local emission sources. The particulate samplings were carried out between 21 March and 12 May 2003 (spring) with prevailing ambient temperature of 4±5°C and total precipitation of 48 mm.

Barcelona (41°23' N, 2°9' E). The site was located on a car park near the city centre. The nearest major road at a distance of 100 m had an average traffic density of 17 000 vehicles/day. On one side, there was a multi-storey building and the canopy of a railway station whilst on the other side there was a park enclosing a zoo. Road traffic and ships in the large harbour, and to some extent the zoo, were considered as the main local emission sources. The sampling campaign was conducted between 28 March and 19 May 2003 (spring) when the ambient temperature and total precipitation were 15±2°C and 10 mm.

Athens (37°58' N, 23°43' E). The site was located near the city centre at a distance of 100 m from the nearest major road with an average traffic density of 30 000 vehicles/day. The site was sparsely enclosed by three- or four-storey buildings. Road traffic, and to some extent construction work, were considered as the main local emission sources. The particulate samplings were carried out between 2 June and 21 July 2003 (summer) with prevailing ambient temperature of 29±4°C and total precipitation of 0 mm.

The sampling duration was 3+4 days per week, with filter exchange usually on Mondays and Thursdays between 10:00 and 12:00 a.m. The general protocol of the PAMCHAR field campaign necessitated to choose these relatively long samplings due to a parallel sampling of large, size-fractionated particulate samples for toxicological cell and animal studies, using a high-volume cascade impactor (Sillanpää et al., 2003). The total number of particulate samplings was 14 in each city. An automatic valve, that was programmed to switch on and off in cycles of 15 min, was installed into the pump line of virtual impactors (VI) in Barcelona and Athens to avoid overloading of the filters.

2.2 Aerosol sampling instruments

The aerosol particulate samples were collected in parallel with two VIs that divide the particulate matter into two size ranges: PM_{2.5} and PM_{2.5–10} (Loo and Cork, 1988). The total sampling flow rates of the VIs were 16.7 l min^{−1} and the upper cut-off of the coarse particles was made with a low volume PM₁₀-inlet similar to the design of Liu and Pui (1981). The particles were collected on polytetrafluoroethylene (PTFE) filters (diameter 47 mm, pore size 3 µm, type FS, Millipore, Ireland) for gravimetric and chemical analysis, and on preheated quartz fibre filters (Pallflex Tissuquartz 2500QAT-UP) for carbon analysis. In the latter VI, a tandem filter collection method (two quartz fibre filters from the same lot in series) was applied for estimation and correction of positive sampling artefacts, i.e. an adsorption of organic gases. In practice, the OC value of backup filter was subtracted from that of front filter. The positive artefact correction has been performed to all the POM results presented in this study.

2.3 Gravimetric and chemical analysis

After sampling, the filters were placed on petrislides and those containing the quartz fibre filters were wrapped inside aluminium foil. All the samples were frozen and sent via express delivery service to the central laboratory of the project at the Finnish Meteorological Institute for gravimetric measurements and chemical analysis.

The PTFE filters were weighed with the same Mettler M3-microbalance (Mettler Instrumente AG, Zurich, Switzerland) before and after sampling. The samples were allowed to stabilize in the weighing room for 15–60 min before weighing, which was shown in separate experiments to be sufficient for both clean and loaded PTFE filters. A criterion for valid weighing was that duplicate mass readings were within 2 µg from each other. The mean±SD relative humidity (RH) and temperature in the weighing room were 22±7% and 23±2°C, respectively, with the exception of RH being 49±8% during weighing the Barcelona and Athens samples. Regardless of different RH, the deliquescence points of the abundant inorganic atmospheric salts were reached neither at 22% nor at 49% (Seinfeld and Pandis, 1998), because the filter samples (stored as frozen) were first melted on closed petrislides and subsequently stabilized at the prevailing condition of the weighing room. The scale and reading of the microbalance were checked daily with internal and standard weights. The electrostatic charges of filters were eliminated with a Po-210 radioactive source.

The quartz fibre filters were analysed using a thermal-optical carbon analyser (TOA; Sunset Laboratory Inc., Oregon). This analysis proceeded in two phases. In the first phase, the OC and carbonate carbon were volatilized in pure helium atmosphere at four temperature steps. During the second phase of the analysis, the carbon remaining on the filter

Table 1. Experimental parameters of the thermal-optical carbon analysis (TOA) method used in this study and those of two well-known methods (NIOSH and IMPROVE).

Carrier gas	This study	NIOSH ^a	IMPROVE ^a
He-1 (OC1)	310°C, 60 s	310°C, 60 s	250°C, 150 s
He-2 (OC2)	480°C, 60 s	475°C, 60 s	450°C, 150 s
He-3 (OC3)	615°C, 60 s	615°C, 60 s	615°C, 250 s
He-4 (OC4)	900°C, 90 s	870°C, 90 s	
He/O ₂ ^b	550°C, 60 s	550°C, 45 s	550°C, 200 s
He/O ₂ ^b	625°C, 60 s	625°C, 45 s	
He/O ₂ ^b	700°C, 45 s	700°C, 45 s	700°C, 160 s
He/O ₂ ^b	775°C, 45 s	775°C, 45 s	
He/O ₂ ^b	850°C, 45 s	850°C, 45 s	850°C, 200 s
He/O ₂ ^b	920°C, 60 s	890°C, 120 s	

^a Sciare et al. (2003)

^b A mixture of 2% oxygen in helium.

was heated in a mixture of oxygen and helium (1:49, V-%) by using six temperature steps. The temperature program used in this study followed the well-known NIOSH program with minor modifications (Table 1). A part of the OC pyrolysed into compounds resembling the EC during heating. An optical correction, i.e. a measurement of the transmittance of laser light through the filter, was applied for a separation of the pyrolysed OC from the EC that was determined as the fraction of carbon that comes out after the transmittance has reached its initial value. The POM is obtained by summing up the OC peaks and pyrolysed OC, and multiplying the sum by a factor of 1.4 (Turpin et al., 2000 and Russell, 2003). An analogous method has been described in detail by Viidanoja et al. (2002).

The carbonaceous material was divided into six thermal fractions labelled as follows: OC1 (310°C), OC2 (480°C), OC3 (615°C), OC4 (900°C), OCP (pyrolysed OC) and EC (sum of EC thermal fractions). C(CO₃) refers to the carbonate carbon.

The PTFE filters were analysed by energy dispersive x-ray fluorescence (ED-XRF) for their total Ca content; by ion chromatography (IC) for water-soluble Ca²⁺, succinate, malonate and oxalate; by liquid chromatography mass spectrometry (LC/MS) for monosaccharide anhydrides (ΣMA=levoglucosan+galactosan+mannosan) and by inductively coupled plasma mass spectrometry (ICP-MS) for As, Cu, Ni, V and Zn. The techniques and their methodological uncertainties have been described elsewhere by Sillanpää et al. (2005).

The CaCO₃ concentrations were converted from those of CO₃^{2−} and Ca, analysed by the TOA and ED-XRF, respectively, using the following equations:

$$[\text{CaCO}_3]_{\text{TOA}} = \frac{M(\text{CaCO}_3)}{M(\text{C}(\text{CO}_3))} [\text{C}(\text{CO}_3)] = 8.334 \times [\text{C}(\text{CO}_3)] \quad (1)$$

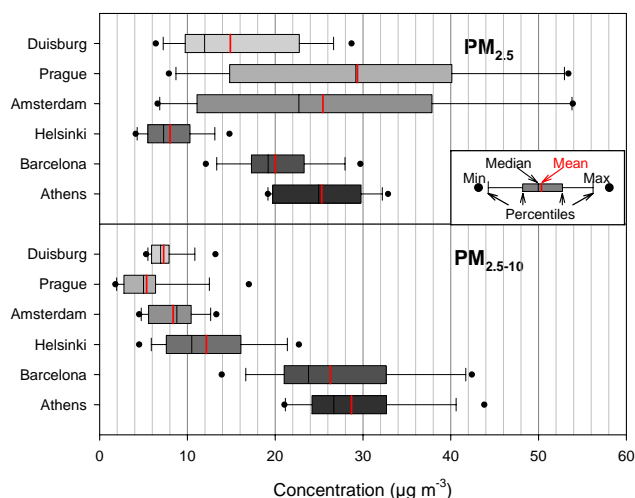


Fig. 1. The arithmetic mean, median and range as well as the 10th, 25th, 75th and 90th percentile values of the mass concentrations of fine ($\text{PM}_{2.5}$) and coarse ($\text{PM}_{2.5-10}$) particulate matter in the six sampling campaigns.

$$[\text{CaCO}_3]_{\text{XRF}} = \frac{M(\text{CaCO}_3)}{M(\text{Ca})} [\text{Ca}] = 2.497 \times [\text{Ca}], \quad (2)$$

where $[\text{C}(\text{CO}_3)]$ and $[\text{Ca}]$ are the mass concentration of carbonate carbon and calcium. The area of the $\text{C}(\text{CO}_3)$ peak in TOA thermograms was manually integrated with the integral start at 210–225 s and end at 250–275 s. The $\text{C}(\text{CO}_3)$ peak was initially localised by comparing the analysis results of the original Athens sample to its duplicate that was decarbonated in HCl fumes as described by Cachier et al. (1989).

2.4 Tracers for assessment of POM sources in $\text{PM}_{2.5}$

An assessment of five common sources of the fine particulate OC content was based on the mass concentration ratio of selected inorganic and organic tracers to POM. The EC is directly emitted from combustion of fossil fuels or/and biomass. It is often regarded as a tracer of local traffic (Song et al., 2001). Several studies have associated Cu and Zn emissions with traffic and metal industries (Pakkanen et al., 2001; Heal et al., 2005; Lim et al., 2005; Song et al., 2001). In the absence of a strong metal industry influence, As can be used as a tracer of coal combustion (NAEI, 2003), and Ni and V as tracers of fuel oil combustion (Song et al., 2001; Kavouras et al., 2001). The sum of three monosaccharide anhydrides ($\sum\text{MA}$; mainly levoglucosan) is known as a good tracer of incomplete biomass combustion (Simoneit et al., 1999; Sillanpää et al., 2005). The small dicarboxylic acids (DA; sum of oxalate, malonate and succinate) are mostly produced in photochemical reactions of anthropogenic organic pollutants in the urban atmosphere (Kawamura and Ikushima, 1993) but they can be also primary emissions from motor vehicle engines (Yao et al., 2004). Here the ratio of DA to POM was used as an indicator of secondary organic compounds.

3 Results and discussion

3.1 $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ mass concentrations

The mass concentrations of $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ during the 7-week campaigns in the six European cities are shown in Fig. 1. The arithmetic mean concentrations were 14.7 and $7.2 \mu\text{g m}^{-3}$ in Duisburg, 29.6 and $5.4 \mu\text{g m}^{-3}$ in Prague, 25.4 and $8.4 \mu\text{g m}^{-3}$ in Amsterdam, 8.3 and $12.8 \mu\text{g m}^{-3}$ in Helsinki, 20.0 and $26.3 \mu\text{g m}^{-3}$ in Barcelona, and 25.3 and $28.7 \mu\text{g m}^{-3}$ in Athens, respectively. The highest mean $\text{PM}_{2.5}$ concentration was measured in Prague during winter and the highest mean $\text{PM}_{2.5-10}$ concentration was measured in Athens during summer, whereas the corresponding lowest values were in Helsinki during spring and in Prague during winter. For comparison (data from local authorities), the annual mean $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ mass concentrations in 2001 were, respectively, as follows: 23.0 and $6.8 \mu\text{g m}^{-3}$ in Duisburg, 7.8 and $7.9 \mu\text{g m}^{-3}$ in Helsinki, and 28.0 and $13.0 \mu\text{g m}^{-3}$ in Barcelona. These two size fractions were not measured in the other three cities but the annual mean PM_{10} mass concentrations in 2001 were 24.5 $\mu\text{g m}^{-3}$ in Prague, 28.9 $\mu\text{g m}^{-3}$ in Amsterdam and 55.5 $\mu\text{g m}^{-3}$ in Athens. Our sampling campaign means were clearly higher than the corresponding annual means for Prague- PM_{10} (43%), Amsterdam- PM_{10} (17%), Helsinki- $\text{PM}_{2.5-10}$ (62%) and Barcelona- $\text{PM}_{2.5-10}$ (100%), suggesting special source-related, episodic or seasonal impacts during the campaigns in these cities. Marginal difference with the historical annual mean value was found for Duisburg- $\text{PM}_{2.5-10}$ (5.9%), Helsinki- $\text{PM}_{2.5}$ (6.4%) and Athens- PM_{10} (−2.7%), but our campaign means were clearly lower than the annual means of 2001 for Duisburg- $\text{PM}_{2.5}$ (−36%) and Barcelona- $\text{PM}_{2.5}$ (−29%).

The mean $\text{PM}_{2.5-10}$ to $\text{PM}_{2.5}$ ratios were clearly lower in Duisburg (0.58), Prague (0.20) and Amsterdam (0.54) than in Helsinki (1.57), Barcelona (1.36) and Athens (1.14). The differences were most likely due to factors related to the season, local emission sources and geographical location. The first three sampling campaigns were carried out during the ‘wet’ and cool seasons favouring a low $\text{PM}_{2.5-10}$ concentration (due to low resuspension) and a high $\text{PM}_{2.5}$ concentration (additional local and regional energy production for heating). The sampling campaigns in Barcelona and Athens were conducted during warmer and drier seasons leading to a lower $\text{PM}_{2.5}$ concentration (semivolatiles in gas phase) and a high $\text{PM}_{2.5-10}$ concentration (resuspension). Road dust episodes, typical phenomena of springtime in Northern Europe, were the reason for elevated $\text{PM}_{2.5-10}$ in Helsinki (Kukkonen et al., 1999). More detailed data on the particulate mass concentrations, meteorology and air quality during the sampling campaigns will be reported elsewhere.

3.2 Mass concentrations of EC and POM in six cities

The POM and EC mass concentrations in $PM_{2.5}$ and $PM_{2.5-10}$ of the six sampling campaigns are shown in Fig. 2. The arithmetic mean POM concentrations in $PM_{2.5}$ varied profoundly between $3.8 \mu\text{g m}^{-3}$ in Helsinki and $15.7 \mu\text{g m}^{-3}$ in Prague, while the corresponding EC concentrations varied much less, i.e. between $0.68 \mu\text{g m}^{-3}$ in Helsinki and $1.6 \mu\text{g m}^{-3}$ in Athens. The mean POM (corrected for $C(\text{CO}_3)$, see Sect. 3.3.1) and EC mass concentrations in $PM_{2.5-10}$ varied in the range of $1.2\text{--}5.0 \mu\text{g m}^{-3}$ and $0.18\text{--}0.28 \mu\text{g m}^{-3}$, respectively. The lowest mean POM and EC in $PM_{2.5-10}$ were observed in Amsterdam, while the corresponding highest concentrations were in Athens. The mean OC concentrations in $PM_{2.5}$ and $PM_{2.5-10}$ of the backup filters varied in the range of $0.32\text{--}1.31$ and $0.12\text{--}0.33 \mu\text{g m}^{-3}$, corresponding to 5.7–19% and 5.8–14% of the OC on the front filters, respectively. The EC contributions were about one tenth of those of the OC, which was also anticipated because of the nonvolatile nature of elemental carbon.

In this study, the POM in both the $PM_{2.5}$ and $PM_{2.5-10}$ was obtained with multiplication of the OC concentration by a factor of 1.4 in each city. This adjustment was made to include a contribution of other elements than the carbonaceous material (OC) of organic compounds to POM (Turpin et al., 2000 and Russell, 2003). The use of this conversion factor should be regarded as a rough means to compensate the limitations of present analytical instruments (e.g. FTIR spectroscopy or GC/MS).

Querol et al. (2004) has reported in their European multi-centre study that the annual mean mass concentration of total carbon (TC; sum of OC and EC) in $PM_{2.5}$ varied in the range of $2\text{--}8 \mu\text{g m}^{-3}$ at urban background sites. Our campaign-mean TC concentrations in $PM_{2.5}$ fell into this range in all other campaigns than Prague ($12.6 \mu\text{g m}^{-3}$). In the study of Querol et al. (2004), the annual mean TC mass concentrations in $PM_{2.5-10}$ were in the range of $0\text{--}1 \mu\text{g m}^{-3}$. Our campaign-mean TCs were between 1.0 and $1.9 \mu\text{g m}^{-3}$, except for the high value of $3.9 \mu\text{g m}^{-3}$ in Athens.

The relative contributions of carbonaceous material to $PM_{2.5}$ and $PM_{2.5-10}$ are shown in Table 2. The POM contributions to $PM_{2.5}$ were very high, ranging from 21% in Barcelona to 54% in Prague, while those to $PM_{2.5-10}$ were generally lower, i.e. from 10% in Barcelona to 27% in Prague. As expected, the EC contributions to $PM_{2.5}$ (5–9%) were higher than those to $PM_{2.5-10}$ (1–6%) in all the six campaigns. Putaud et al. (2004) have made a meta-analysis of the annual mean black carbon (BC) and POM contributions based on measurements at urban background sites of eight European cities. The mean BC contributions to $PM_{2.5}$ and $PM_{2.5-10}$ were 8% and 3%, respectively, which agrees well with our present results. In contrast, their annual mean POM contributions to $PM_{2.5}$ and $PM_{2.5-10}$ were only 22% and 8%, i.e. values similar to our smallest campaign-means and about one-third to one-half of our largest campaign-means. De-

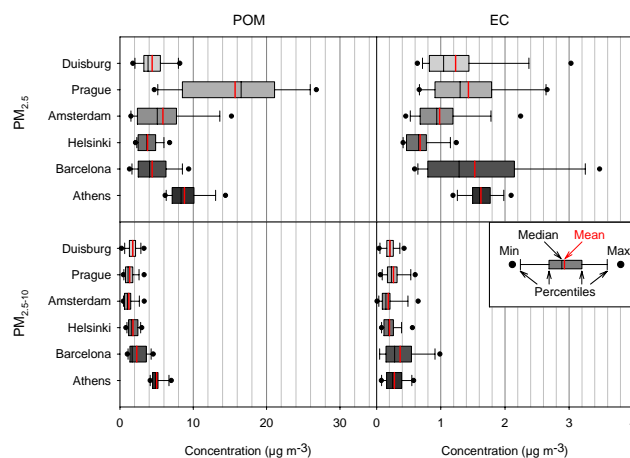


Fig. 2. The arithmetic mean, median and range as well as the 10th, 25th, 75th and 90th percentile values of the particulate organic matter (POM) and elemental carbon (EC) concentrations in $PM_{2.5}$ and $PM_{2.5-10}$ of the six sampling campaigns.

spite the differences in sample collection and analysis techniques between our study and the other European studies, this finding suggests that the selected campaign periods of public health concern in several cities (e.g., Prague, Athens, Helsinki) were associated with a relatively high POM content.

It is worthwhile noting that the EC and OC results are dependent on the method used in the thermal-optical carbon analysis. Chow et al. (2001) have shown that the NIOSH and IMPROVE methods (Table 1) are equivalent for total carbon but the EC of NIOSH (usually a smaller fraction of TC) is typically less than half of the value of the EC of IMPROVE. A reasonable estimate for the EC probably lies somewhere between the values given by these two methods (Sciare et al., 2003). We used a slightly modified NIOSH method (see Table 1) and, therefore, the EC concentrations may be somewhat underestimated and the OC concentrations slightly overestimated in the present study.

The mean $PM_{2.5-10}$ to $PM_{2.5}$ ratio of the EC ranged between 0.17 and 0.29. These low ratios indicate that the EC existed mainly in $PM_{2.5}$, which has been observed in many European urban environments (Viidanoja et al., 2002; Salma et al., 2004). The mean $PM_{2.5-10}$ to $PM_{2.5}$ ratio of POM had a much larger range than that of the EC, being 0.094 for Prague, 0.24 for Amsterdam, 0.45 for Duisburg, 0.50 for Helsinki, 0.56 for Barcelona and 0.59 for Athens. The ratios were lower for sampling campaigns with a lower mean ambient temperature and a higher precipitation (see Sect. 2.1).

3.3 Assessment of POM and EC sources in $PM_{2.5}$

The Pearson correlation coefficients between the total mass concentration, POM and EC in $PM_{2.5}$ and $PM_{2.5-10}$ are shown in Table 3. The fine POM concentration had a high

Table 2. The relative contribution (%) of particulate organic matter (POM) and elemental carbon (EC) to the total mass (PM) in PM_{2.5} and PM_{2.5–10} as well as the ratio of organic carbon (OC) to EC in the six sampling campaigns.

		POM/PM (%)			EC/PM (%)			OC/EC			BU/F-OC ^a (%)
		Mean (SD)	Min	Max	Mean (SD)	Min	Max	Mean (SD)	Min	Max	Mean±SD
PM _{2.5}	Duisburg	31 (6)	21	38	9.0 (3.1)	4.7	15	2.7 (0.9)	1.7	5.2	16±7
	Prague	54 (4)	48	60	5.7 (2.7)	1.3	11	8.7 (6.0)	3.6	27	6±2
	Amsterdam	23 (4)	19	29	5.4 (3.4)	1.7	13	4.3 (2.6)	1.2	9.8	12±5
	Helsinki	46 (6)	34	57	8.4 (1.8)	4.5	11	4.0 (0.9)	2.8	6.3	14±3
	Barcelona	21 (11)	8.9	49	7.6 (4.5)	3.1	18	2.1 (0.5)	1.5	3.1	17±3
	Athens	35 (4)	30	47	6.8 (1.4)	4.9	9.4	3.9 (0.9)	2.7	5.4	19±3
PM _{2.5–10}	Duisburg	24 (8)	3.4	37	2.9 (1.2)	0.48	5.0	9.1 (9.8))	0.7	39	14±19
	Prague	27 (7)	16	41	5.5 (2.6)	2.2	11	3.9 (1.5)	2.0	7.3	10±5
	Amsterdam	15 (8)	5.6	28	2.3 (1.5)	0.06	5.4	11 (21)	3.4	84	12±3
	Helsinki	15 (4)	11	25	1.6 (0.6)	0.84	2.7	7.1 (2.3)	3.8	13.6	8±3
	Barcelona	10 (6)	2.7	23	1.1 (0.9)	0.15	3.2	9.0 (5.5)	4.1	18.1	9±4
	Athens	24 (3)	19	30	1.0 (0.4)	0.23	1.9	24 (17)	9.5	62	6±1

^a BU/F-OC is the ratio of OC on backup filter to OC on front filter.

Table 3. The Pearson correlation coefficients (*r*) between the total particulate mass, POM, and EC in PM_{2.5} and PM_{2.5–10}.

	Duisburg	Prague	Amsterdam	Helsinki	Barcelona	Athens
PM _{2.5} vs. PM _{2.5–10}	0.280	0.554	−0.128	0.584	0.295	0.717
EC _{2.5} vs. EC _{2.5–10}	0.524	0.379	0.875	0.810	0.884	0.348
POM _{2.5} vs. POM _{2.5–10}	0.542	0.661	0.897	0.498	0.824	0.800
PM _{2.5} vs. EC _{2.5}	0.553	0.360	0.664	0.722	0.341	0.405
PM _{2.5} vs. POM _{2.5}	0.844	0.987	0.959	0.897	0.567	0.860
EC _{2.5} vs. POM _{2.5}	0.672	0.436	0.762	0.790	0.945	0.517
PM _{2.5–10} vs. EC _{2.5–10}	0.352	0.822	0.208	0.696	−0.087	0.470
PM _{2.5–10} vs. POM _{2.5–10}	0.651	0.935	0.263	0.904	−0.073	0.831
EC _{2.5–10} vs. POM _{2.5–10}	0.198	0.828	0.926	0.813	0.870	0.659

High correlations ($r \geq 0.80$) bolded.

correlation ($r=0.84–0.99$) with the PM_{2.5} concentration in all cities except for Barcelona ($r=0.57$) where the POM had the smallest contribution to PM_{2.5}. However, the POM and EC in PM_{2.5} of Barcelona were highly intercorrelated ($r=0.95$), which together with the lowest OC to EC ratio (see next paragraph) suggests that they had a common dominant source different from the other cities, e.g. fuel oil combustion in numerous ship engines at the large harbour. The fine EC concentration had a relatively low correlation ($r=0.34–0.72$) with the PM_{2.5} concentration in all the six campaigns, but it correlated highly ($r=0.81–0.88$) with the coarse EC in Amsterdam, Helsinki and Barcelona, suggesting impacts from local combustion sources not only to PM_{2.5} but also to PM_{2.5–10}. Only in the winter campaign of Prague, the coarse EC concentration had a high correlation ($r=0.82$) with the PM_{2.5–10} concentration, which refers to local incomplete combustion processes such as residential heating with solid fuels. The

coarse POM concentration correlated highly ($r=0.83–0.94$) with the PM_{2.5–10} concentration in Prague, Helsinki and Athens, which reflects its highly variable anthropogenic and natural sources in different urban environments and seasons (Table 3).

The OC to EC ratios in PM_{2.5} were in the range of 2.1–4.3 in Barcelona, Duisburg, Athens, Helsinki and Amsterdam, but it was much higher (8.7) in Prague (Table 2). Na et al. (2004) have reviewed some of the reported OC to EC ratios in relation to a variety of combustion sources. A low OC to EC ratio has been associated with traffic sources (2.2 and 0.8 for light-duty gasoline and heavy-duty diesel vehicles, respectively), whereas residential heating (wood combustion 4.15 and natural gas home appliance 12.7), forest fire (14.5) and dust from paved roads (13.1) have shown remarkably higher ratios.

Figure 3 shows the mass concentration ratios in $\text{PM}_{2.5}$ of the selected inorganic and organic tracers (see Sect. 2.4.) of five common sources of organic material to POM.

Traffic. Road traffic has certainly a substantial impact on the POM concentration in $\text{PM}_{2.5}$ of all the six urban background sites. As assessed from the ratio of EC, Cu and Zn to POM, its relative impact was largest in Barcelona and Duisburg, and smallest in Prague (Fig. 3). However, the high ratios of Cu and Zn to POM in Duisburg were likely to be at least partially due to emissions from the large metal industries in the Ruhr area.

Coal combustion. According to the As to POM ratio in $\text{PM}_{2.5}$, the contribution of coal combustion emissions was higher in Prague, Duisburg, Amsterdam and Barcelona than in Helsinki and Athens (Fig. 3). The first three cities had sampling campaigns during the cold and wet seasons, which means that their findings can be explained by increased local and regional residential heating, and larger-scale energy production, with coal. In Barcelona, the impact may be derived from the emissions from coal plants located nearby the city (Rodríguez et al., 2002).

Fuel oil combustion. As assessed from the ratios of Ni and V to POM, the contribution of fuel oil combustion was clearly highest in Barcelona followed by Helsinki, Amsterdam and Athens (Fig. 3). Ships in the harbours of these cities can be regarded as the major source, because it seemed to have a low impact in the inland cities of Duisburg and Prague. The large metal industries in the Ruhr area probably elevated the Ni contribution to $\text{PM}_{2.5}$ of Duisburg to some extent, but the V contribution remained low. The ratio of Ni to V in $\text{PM}_{2.5}$ is expected to be around 0.38 in relation to impact from fuel oil combustion (Kavouras et al., 2001), which was close in all other cities (0.27–0.45) than Duisburg (0.57) (Fig. 3).

Biomass combustion. According to the ΣMA to POM ratio, the contribution of biomass combustion was clearly higher in Prague, Amsterdam and Duisburg than in Helsinki, Barcelona and Athens (Fig. 3). The differences can be explained by an impact from local or regional residential heating, since the three former campaigns were carried out during the cold and wet seasons. In Prague, the very high mass concentration of POM in $\text{PM}_{2.5}$ (Fig. 2) as well as the above described high correlations of both the coarse EC and POM with the $\text{PM}_{2.5-10}$ concentration (Table 3) suggest a larger contribution from local biomass combustion than in Amsterdam and Duisburg.

Secondary POM. The DA to POM ratios in the spring-time and summertime campaigns of Helsinki, Barcelona and Athens were 2–9 times higher than those in the autumn and winter campaigns of Duisburg, Prague and Amsterdam (Fig. 3). The likely reason for this difference is enhanced photochemical oxidation of organic compounds in the spring and summer (Kamamura and Ikushima, 1993).

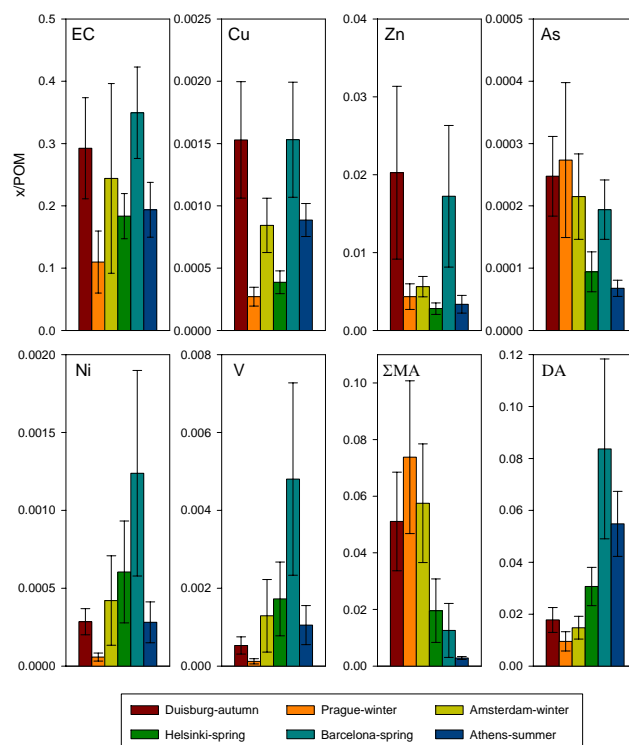


Fig. 3. The mass concentration ratios of the selected tracers of common emission sources of organic material to POM in $\text{PM}_{2.5}$. The values are means \pm SD of 14 samples collected during a 7-week sampling campaign in each city. See text for further explanation.

3.4 Analysis of thermal fractions

3.4.1 Carbonate in atmospheric particles

The carbonate-carbon ($\text{C}(\text{CO}_3)$) can interfere with the TOA analysis during the OC4 step (Fig. 4) and cause a positive artefact to the OC concentration (Sciare et al., 2003). In this study, $\text{C}(\text{CO}_3)$ could be quantified in the $\text{PM}_{2.5-10}$ samples of Barcelona and Athens, but it was not detected either in the $\text{PM}_{2.5-10}$ samples of the other four cities or in the $\text{PM}_{2.5}$ samples of any city. The mean $\text{C}(\text{CO}_3)$ to OC ratio in $\text{PM}_{2.5-10}$ was 0.17 in Barcelona and 0.53 in Athens, which indicates that the OC (and subsequently POM) concentration in certain situations can be grossly overestimated without a subtraction of the $\text{C}(\text{CO}_3)$. We subtracted the $\text{C}(\text{CO}_3)$ concentration from the OC4 and total OC concentration before conversion of the OC results to POM shown in Sect. 3.2.

A time-series of the CaCO_3 concentration in the $\text{PM}_{2.5-10}$ samples from Athens and Barcelona is shown in Fig. 5. The campaign mean (range), based on Eq. (1), was 15.9 (9.8 – 29.2) $\mu\text{g m}^{-3}$ for Athens, whereas the corresponding value for Barcelona was 2.6 (0.3 – 6.3) $\mu\text{g m}^{-3}$. These concentrations accounted for $55(\pm 8)\%$ and $11(\pm 9)\%$ of the $\text{PM}_{2.5-10}$ concentration in Athens and Barcelona, respectively. There was a high linear correlation ($r = 0.91$) and the slope close

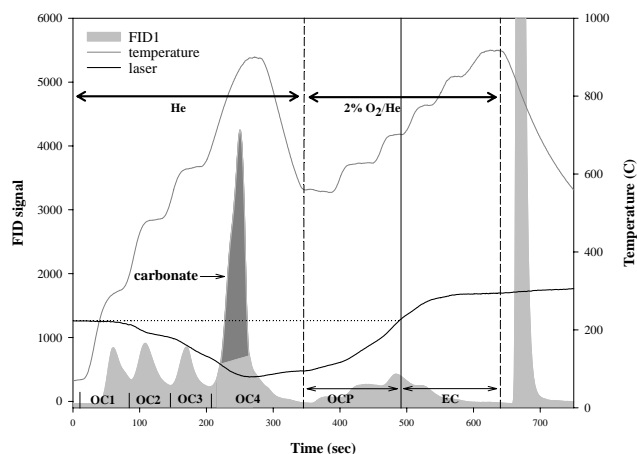


Fig. 4. Example of the temperature program in the thermal-optical carbon analysis (TOA) and a manually integrated carbonate $\text{C}(\text{CO}_3)$ peak in the present study ($\text{PM}_{2.5-10}$ sample #14 from Athens). See text and Table 1 for other explanations.

to unity between the $[\text{CaCO}_3]_{\text{TOA}}$ and $[\text{CaCO}_3]_{\text{XRF}}$ concentrations (based on Eqs. (1) and (2)) in Athens, and a significant trend in Barcelona (Pearson's $r=0.61$) although the molar equivalent concentration of CO_3^{2-} was lower than that of Ca (Fig. 5). This indicates that the coarse Ca appeared exclusively as CaCO_3 in Athens, whereas the coarse Ca in Barcelona existed partly in other forms (e.g. as oxide). A similar conclusion has been drawn by Bardouki et al. (2003) who discovered in ion balance calculation that the coarse Ca was strongly associated with $\text{C}(\text{CO}_3)$ (a molar ratio close to 1) during summertime in the Eastern Mediterranean.

Figure 6 shows the portion of crustal elements in the soil-derived coarse particles of the six sampling campaigns. These data further support the view of CaCO_3 appearance in the $\text{PM}_{2.5-10}$ samples of Athens and Barcelona. Calcium had its largest contributions to the $\text{PM}_{2.5-10}$ of Athens and Barcelona, whereas Al and Si had major contributions in the other four cities. In addition, the fine-to-coarse ratio of total Ca was lower in Barcelona (0.064) and Athens (0.068) than in the other four cities (0.086–0.183), indicating a strong coarse particle dominance in Ca distribution. The contribution of water-soluble Ca^{2+} to the total amount of Ca was determined on the basis of results from the IC (soluble fraction) and ED-XRF (total amount) analyses. A relatively low contribution of total Ca to $\text{PM}_{2.5-10}$, together with its high water-solubility, in Duisburg, Prague and Amsterdam indicates that Calcium appeared mainly as water-soluble salts (e.g. oxide or sulphate) and not as poorly water-soluble salts like CaCO_3 . On the contrary, a high contribution of insoluble Ca, together with a low Si contribution, to $\text{PM}_{2.5-10}$ agrees well with the appearance of CaCO_3 in Athens and Barcelona. In Helsinki, the relatively high insoluble Ca (about 50% of total), together with a high Si contribution, to $\text{PM}_{2.5-10}$ suggests an appearance of other water-insoluble compounds such as Calcium silicates in the absence of $\text{C}(\text{CO}_3)$ (Fig. 6).

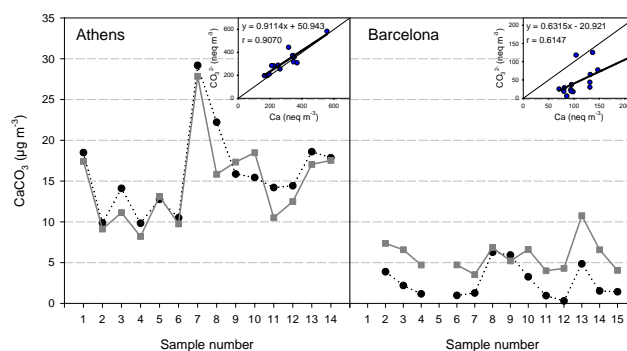


Fig. 5. Time-series of the mass concentration of CaCO_3 in $\text{PM}_{2.5-10}$ of Athens and Barcelona. The black dotted line is based on the CO_3^{2-} content analysed by the TOA, and the grey continuous line is based on the Ca content analysed by the ED-XRF. The linear regressions for the molar equivalent concentrations of Ca (x-axis) and CO_3^{2-} (y-axis) are shown in the right upper corners of the panels for the two campaigns.

3.4.2 Thermal fractions of OC in $\text{PM}_{2.5}$

The thermograms, i.e. the output from the TOA analysis of the OC and EC in the six-city samples, are comparable with each other, because the sampling devices, protocols and the analytical method were identical. The mean mass portions of the five OC thermal fractions in $\text{PM}_{2.5}$ – labelled OC1, OC2, OC3, OC4 and OCP – varied in the range of 26–33%, 6–10%, 7–10%, 9–22% and 29–50%, respectively (Fig. 7). The differences in the mass portions were relatively small between the cities. However, there was a trend that the pyrolysed OC fraction was higher (OCP 50%) in Prague than in the other cities (29–41%) and, vice versa, the OC peaks at temperature steps of 480, 615 and 900°C (i.e. OC2–OC4) were somewhat smaller in Prague than in the other cities.

The OC concentration in $\text{PM}_{2.5}$ correlated inversely with the OC1 ($r=-0.32$ to -0.75), OC2 ($r=-0.022$ to -0.58), OC3 ($r=-0.51$ to -0.69) and OC4 ($r=-0.31$ to -0.94) in all the six-city data, whereas the OCP had a relatively high positive correlation with the OC ($r=0.70$ to 0.93). This pattern in results suggests a too short residence time at each temperature step of the TOA method, which may be partly a consequence of the 3- to 4-day sampling duration and relatively large masses of $\text{PM}_{2.5}$ particles on our filters. In any case, the too short residence time at temperature steps increases charring of the OC (Yu et al., 2002), irrespectively of the organic composition of particulate samples. The transmittance of laser light through the filter gradually decreases, which suggests that a part of OC is pyrolysed during each OC temperature step (OC1–OC4).

The dominating thermal fraction from the $\text{PM}_{2.5}$ backup filters was OC1 (56–62%), whereas the OC2–OC4 (10–16%) and OCP (0–3%) were found only in minor quantities. The thermogram profiles from the six-city samples were similar

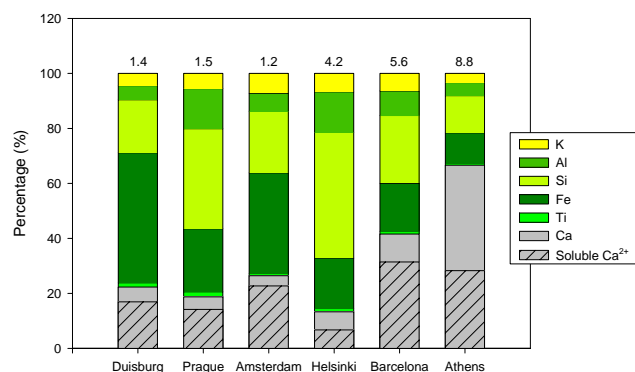


Fig. 6. The relative contribution (%) of crustal elements (Ca, Ti, Fe, Si, Al and K) to the soil particles in $\text{PM}_{2.5-10}$. The value above the bar indicates to the sum of mean concentrations ($\mu\text{g m}^{-3}$) of the crustal elements during the six sampling campaigns. The portion of water-soluble Ca^{2+} from the total Ca is shown as a striped bar.

to each other, irrespective of the geographical location or season. In this study, the OC on the backup filter was anticipated to be comprised of adsorbed organic gases, but some part of it may have been formed via evaporation of semivolatile organics from particles collected on the front filter (Turpin et al., 2000). Regardless of its origin (positive or negative artefact), the OC on backup filter seemed to be easily volatile (i.e. a large OC1).

Only very limited conclusions can be drawn from the chemical content of thermal fractions, because the evolution of organic components depends on several factors. First, the presence of some catalytically active inorganic salts such as Na^+ and K^+ (Novakov and Corrigan, 1996) or ammonium sulphate and phosphate (Yu et al., 2002) can increase the combustion rate of certain compounds (Novakov and Corrigan, 1996) or the charring of insoluble organic materials (Yu et al., 2002). Second, as mentioned above, the too short steps of the temperature program cause overlapping of the OC peaks and increase the charring. Third, organic gases can be adsorbed on quartz filter with more than a single binding energy (Kirchstetter et al., 2001), which results in an appearance of a certain compound in more than one thermal fraction.

4 Conclusions and implications

The advantages of this study were as follows: 1) all the samples were collected using the same sampling devices and following a uniform protocol, 2) the samples were analysed with the same TOA method in one central laboratory, and 3) the long sampling duration and the use of filters from one manufacturing lot improved the accuracy of the tandem quartz filter subtraction method. All of these factors improved the comparability of the EC, OC and POM results between the six contrasting sampling campaigns. However, we

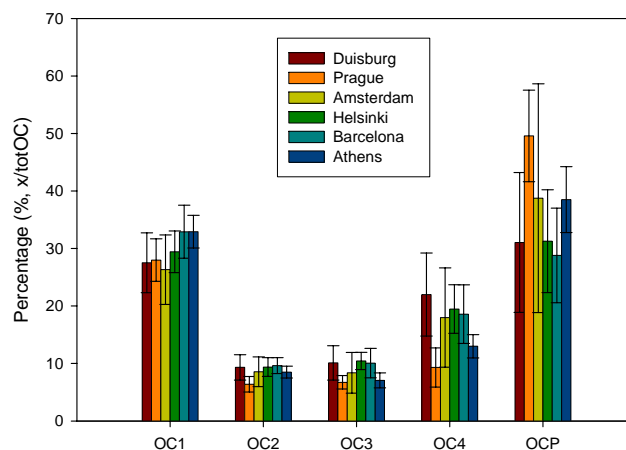


Fig. 7. The mean \pm SD relative contributions (%) of the four OC thermal fractions (OC1–OC4) and pyrolysed OC (OCP) to the total OC in $\text{PM}_{2.5}$ of the six sampling campaigns.

could not reliably separate the four thermal fractions (OC1–OC4) and the pyrolysed OC from each other, because the residence time in our modified NIOSH programme of TOA was too short for the rather large amounts of particles on our filters. Moreover, the long sampling duration may have increased evaporative OC losses from collected particles.

Our present validation indicates that carbonate ($\text{C}(\text{CO}_3)$) in $\text{PM}_{2.5-10}$ can be reliably quantified from the TOA thermograms and subtracted from the OC with the help of the described integration. This simple method can be used as an alternative for the more time-consuming HCl pre-treatment method (Cachier et al., 1989). In a future study, it would be worth while investigating, how $\text{C}(\text{CO}_3)$ behaves in the IMPROVE thermal program. As CaCO_3 decomposes at a relatively high temperature of about 800°C , its appearance in particulate samples would probably lead to an overestimation of the EC concentration compared to the NIOSH programme.

It is obvious that combustion emissions from vehicle engines affected the POM content in $\text{PM}_{2.5}$ of all the six sampling campaigns. However, our analysis of the sources of organic material in POM revealed some important differences. The $\text{PM}_{2.5}$ of Prague (winter) had obviously large impacts on POM from local residential heating with solid fuels (biomass, coal), while the POM in $\text{PM}_{2.5}$ of Amsterdam (winter) and Duisburg (autumn) might be mainly impacted by regional aerosols from the same origins. The POM in $\text{PM}_{2.5}$ of Barcelona (spring) seemed to have the largest relative contribution of all the six campaigns from fuel oil combustion, most likely in ships at the large harbour. Finally, the POM in $\text{PM}_{2.5}$ of Barcelona (spring) and Athens (summer) seemed to have a much larger contribution than the other campaigns from secondary organic compounds formed in photochemical oxidative reactions in the atmosphere. The on-going toxicological studies will clarify the health significance of these findings.

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